CHROM. 3330

DERIVATOGRAPHIC STUDIES OF GAS-CHROMATOGRAPHIC PARTITION LIQUIDS. II

G. LIPTAY
Institute for Applied Chemistry of the Technical University, Budapest XI (Hungary)
S. BÉKÁSSY*
Institute for Organic Chemistry of the Technical University, Budapest XI (Hungary)
AND
J. TAKÁCS
Institute for General and Analytical Chemistry of the Technical University, Budapest XI (Hungary)
(First received October 5th, 1967; modified October 31st, 1967)

SUMMARY

Further derivatographic investigations were made for the purpose of elucidating some problems concerning column fillings used in gas chromatography. New data are given for the upper temperature limit of applicability of column fillings. The interactions between support and partition liquid, and partition liquid mixtures were studied.

In an earlier paper[1] we reported a derivatographic investigation[2] of gas-chromatographic supports, partition liquids and fillings. In our present paper we wish to report the results of further derivatographic studies of the above materials. So far only thermal methods have been used to investigate the above systems.

Our experiments were made with a Paulik-Paulik-Erdey Orion-Gyem 676 Type derivatograph, at a heating rate of 3°/min, with samples of about 300 mg. Derivatographic measurements were carried out in air, or in a stream of bomb nitrogen at a flow rate of 20 l/h.

The dependence of the upper temperature limit of usefulness of the column filling on the amount of coating was first studied. After selecting the model (Apiezon L–Chromosorb W, 60–80 mesh) the thermoanalytical curves of the pure components were determined (Fig. 1).

As shown by the figure, the solid support studied is of constant weight practically up to 500°, no transformation being shown even by the DTA curve which reflects enthalpy changes, therefore the support does not undergo any structural change in the temperature range studied. The partition liquid is of constant weight up to 240°. Above this temperature decomposition processes also begin to occur in addition to the increase in vapour pressure, as shown by the exothermic nature of the DTA curve. It must be pointed out that at 500° about 6 % of the partition liquid remains on the support under the given experimental conditions as a product of cracking.

* Present address: Institute for Organic Chemical Technology of the Technical University, Budapest, Hungary.

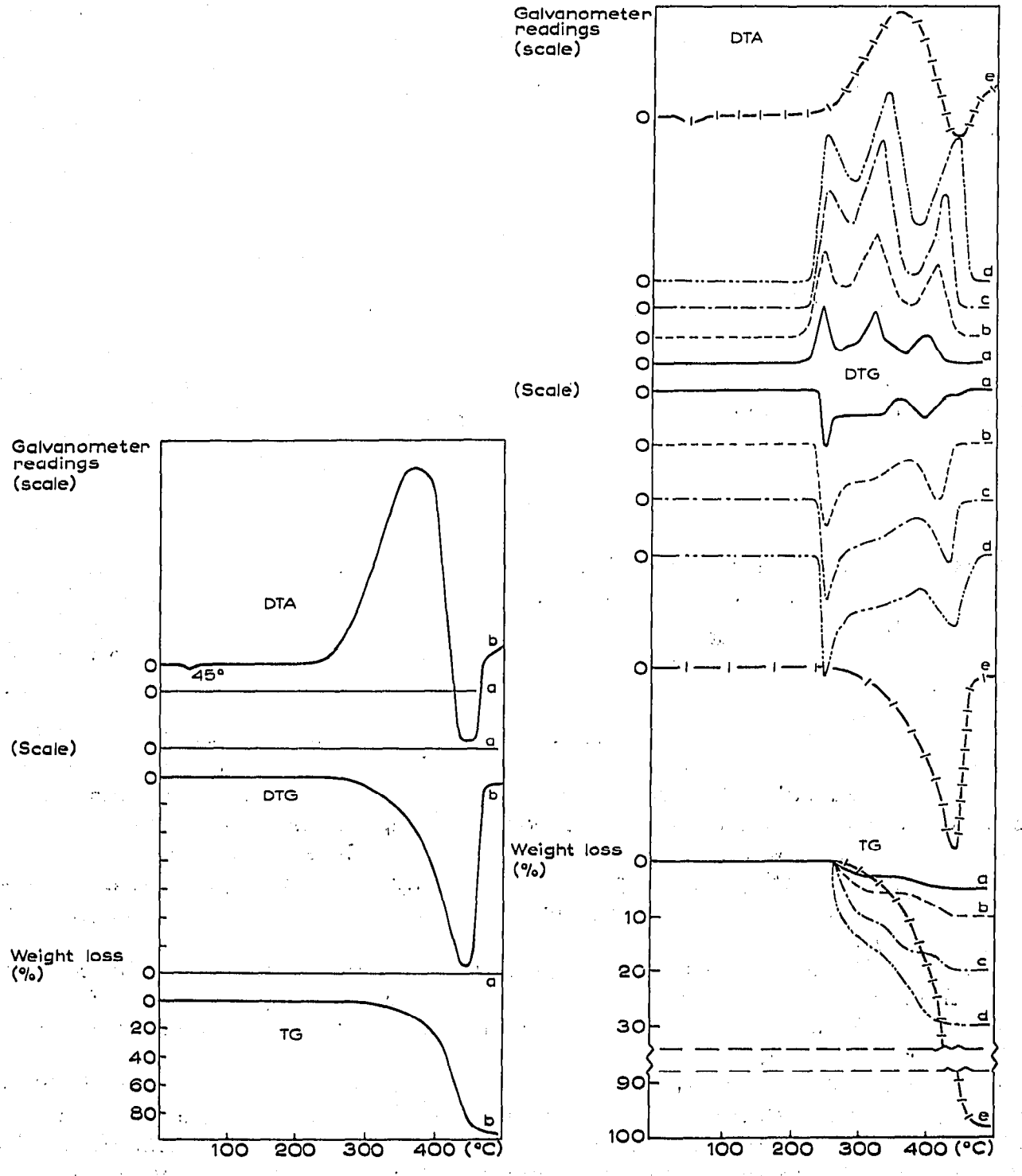

Fig. 1. Derivatograms of Chromosorb W 60–80 mesh (a) and Apiezon L (b). TG = thermogravimetric; DTG = derivative thermogravimetric; DTA = differential thermoanalytical.

Fig. 2. Derivatograms of Apiezon L–Chromosorb W fillings with various percentages of Apiezon coating (a = 5%, b = 10%, c = 20%, d = 30%), and of pure Apiezon L (e). TG = thermogravimetric; DTG = derivative thermogravimetric; DTA = differential thermoanalytical.

This phenomenon must be taken into consideration in each case when one wishes to determine the concentration of coating, and is also of importance in gas chromatography, because, if the column is over-heated the cracking products remaining on the support may make the prolonged use of support impossible.

The derivatograms of column fillings with different concentrations of liquid phase (2–50 %) were then recorded. Fig. 2 shows the thermoanalytical curves (a,b,c,d) of fillings with those concentrations of Apiezon L most frequently used in gas chromatography and also the derivatogram of the pure partition liquid (e).

It was found that for the selected pair of model substances the concentration of the coating has very little effect (5–10°) on the upper temperature limit of applicability of the partition liquid, and the temperature limits found for fillings with different concentrations of coating were practically the same as that found for pure Apiezon L, 240°. The shapes of the derivatograms found for the pure partition liquid and the fillings, however, are rather different in that the thermogravimetric (TG) curve for the fillings has a fraction which suddenly declines while that of the pure partition liquid only smoothly declines. This can be explained by the fact that oxidation processes have an important role in the case of prepared fillings. The absorption of activation energy necessary for oxidation at a given temperature causes the sudden and rapid decomposition of the whole of the partition liquid spread over a large surface.

In order to study other aspects of the interaction between the solid support and the partition liquid, similar fractions (60–80 mesh) of different supports were coated with similar amounts (5 %) of Apiezon L and the thermoanalytical curves of these fillings taken. A few characteristic derivatograms of the many obtained are presented in Fig. 3. The derivatogram of the pure partition liquid (see Fig. 1) is also necessary for the evaluation of the curves.

As shown by Fig. 3 a considerable difference exists between the results obtained with Chromosorb P and Chromosorb P-AW, and those obtained for other carriers. For the two carriers mentioned the upper temperature limit of usefulness was found to be higher by about 40° (280°) than that for all the other carriers studied. This phenomenon is probably due to the differences in the specific surface areas of the supports. Data given by the manufacturer[3] are listed in Table I.

TABLE I

Support	*Specific surface area* (m^2/g)	*Free fall density* (g/cm^3)
Chromosorb P	4.0	0.38
Chromosorb W	1.0	0.18
Chromosorb G	0.5	0.47

Owing to the considerably higher specific surface area of Chromosorb P type supports, the adsorption effect of the support is the one prevailing, which reduces the extent of distillation, and increases the activation energy of oxidation. In the same series of experiments the influence of the pretreatment of Chromosorb W type supports on the upper temperature limit of applicability of partition liquids was also investi-

gated. The same results were obtained for the carrier washed with acid (W-AW) as for that washed with acid and treated with silane (W-AW-ST) and as for untreated carrier.

The derivatographic curves of the pure carriers were also necessary for the evaluation of the series of experiments mentioned above. No very great differences were found between the different types of support studied. The weight of most

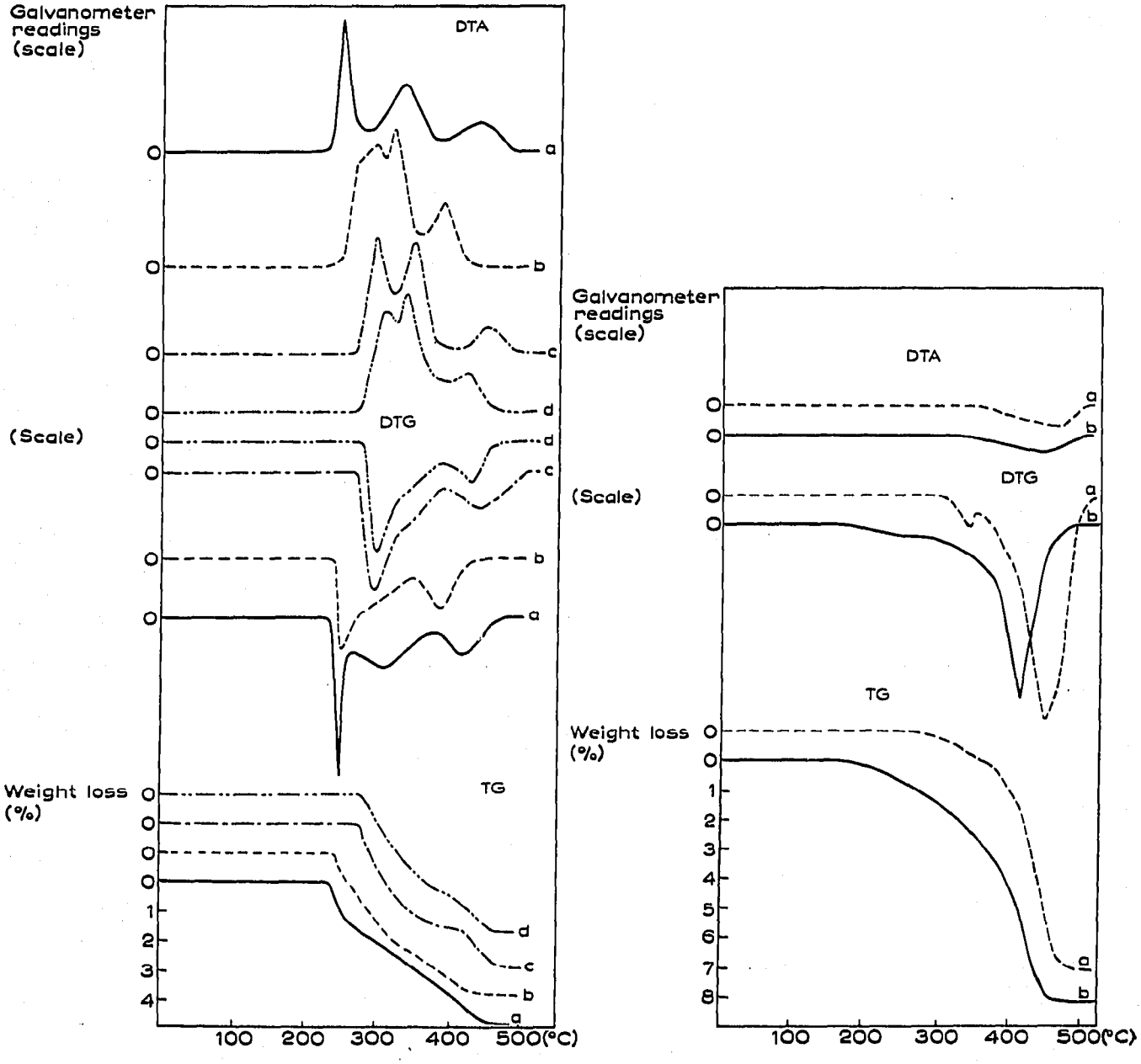

Fig. 3. Derivatograms of Chromosorb W-AW-ST (a), Chromosorb G (b), Chromosorb P-AW (c) and Chromosorb P (d) coated with 5 % Apiezon L. TG = thermogravimetric; DTG = derivative thermogravimetric; DTA = differential thermoanalytical.

Fig. 4. Derivatograms of Chromosorb G coated with 8 % Silicone Oil 550 (a) and of Chromosorb G coated with 7.6 % Silicone Oil 550 + 0.4 % stearic acid (b). TG = thermogravimetric; DTG = derivative thermogravimetric; DTA = differential thermoanalytical.

carriers was found to decrease continuously by 0.3–1.5 % between 20 and 500°. Therefore the heating of the supports before preparing the filling to be used at temperatures (450–500°) higher than the usual seems to be expedient.

The possibility of using the derivatographic method to determine the degree of exhaustion of column fillings is of special importance for studying columns used for preparative purposes. In this case the column is exhausted quickly because of the greater demands made (longer continual use, high flow rate, etc.). Chromosorb G column filling coated with 8 % Silicone Oil 550 was found to lose 0.5 % coating liquid during 6 h use at 170°. The derivatographic method was also used to study the problems concerning the upper temperature limit of applicability of partition liquid mixtures. The derivatograms of fillings prepared with Silicone Oil 550 and Apiezon L, modified with stearic acid (0.4–1.0 %), are presented in Figs. 4 and 5, respectively. It has been found that stearic acid reduces the temperature limit of use of Silicone Oil 550 considerably (by about 30°), and there are also differences in the shape of the curves.

The above phenomenon is even more marked with the partition liquid mixture containing Apiezon L, as shown by Fig. 5. Here the temperature limit was reduced by stearic acid by about 70°.

In future we wish to study the phenomena discussed in our present paper more generally and to interpret them in more detail.

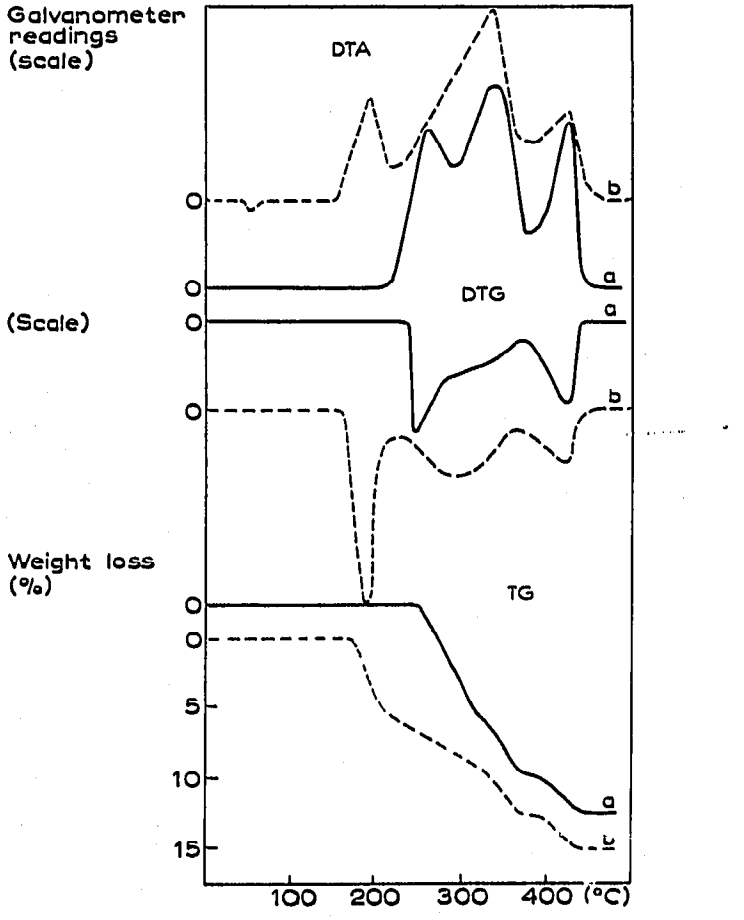

Fig. 5. Derivatograms of Chromosorb P coated with 15 % Apiezon L (a), and of Chromosorb P coated with 14 % Apiezon L + 1 % stearic acid (b). TG = thermogravimetric; DTG = derivative thermogravimetric; DTA = differential thermoanalytical.

ACKNOWLEDGEMENT

We wish to express our thanks to Miss E. SZABÓ for helping us with our experiments and drawing the figures.

REFERENCES

1 G. LIPTAY AND J. TAKÁCS, *J. Chromatog.*, 24 (1966) 22.
2 F. PAULIK, J. PAULIK AND L. ERDEY, *Z. Anal. Chem.*, 160 (1958) 241.
3 *Johns-Manville Bulletin FF-133A.*